

A Brief Look At Some of The Chemicals Used In Darkroom Photographic Chemistry

Developers are made up of four basic components:

- Developing agent.
- Preservative, which slows the rate of developer oxidation.
- Accelerator, which energizes the developer.
- Restrainer, which restricts the formation of excessive fog and/or slows the rate of development.

All four of these components are necessary for the development process to be successful. Often, however, one chemical will serve more than one function. For example, sodium sulfite is usually used as a preservative to prevent oxidation. However, in the film developing formula Kodak D-23 the large amount of sodium sulfite (100.0 grams) serves to create an environment sufficiently alkaline that the developing agent, metol, can reduce the silver halide without an additional accelerator. As development progresses, soluble bromide is precipitated out of the film, acting as an effective restrainer. D-23 has only two chemicals - metol and sodium sulfite - yet as a developer it has all four of the required components!

DEVELOPING AGENTS =

For the non-chemist, development is a reduction process. Silver halide¹ crystals are selectively reduced, through the action of a developer, to metallic silver. In order to be reduced, the silver halide must first be exposed to light. Exposure to light changes its electrical charge and makes it sensitive to the action of the developer. When light is sharply focused by a lens, on film or paper, certain areas receive more exposure than others. The more light an area receives, the more silver halide is affected and subsequently reduced to metallic silver. The more metallic silver in an area of the film or paper, the darker it appears.

There are many chemical agents that will reduce silver halide to metallic silver, but developing agents are a special kind of reducing agent because they act only on silver halide that has been exposed to light.

The following are the four most common developing agents in use today:

- Ascorbic acid
- Hydroquinone
- Metol
- Phenidone™

Other agents more commonly used in the past are as follows:

- Amidol
- Chlorhydroquinone
- Glycin
- Para-Aminophenol hydrochloride
- Para-Phenylenediamine (ppd)
- Pyrocatechin (catechol)
- Pyrogalllic acid (pyro)

All of the above developing agents have unique characteristics, and some have a special purpose. The shortening of the list of modern developing agents has more to do with ease of manufacture, storage, and shipping than it does with their usefulness.

The superadditive effects of hydroquinone, metol, Phenidone, and ascorbic acid (see discussion of superadditivity later in this chapter) has also added to their popularity with manufacturers. Developing agents for film can be used for paper and vice versa. In practical terms, some developing agents are more advantageous to use in one process than another. For example, ppd is better suited for film development than for paper development, while chlorhydroquinone is better suited for paper than film. Hydroquinone, metol, ascorbic acid, and Phenidone are well suited for either film or paper. This is an additional reason they are preferred by manufacturers.

It is worthwhile to familiarize yourself with the brief description of each developing agent in Appendix 3: Pharmacopoeia.

Superadditivity =

The phenomenon known as superadditivity plays an important role in many film developers. Superadditivity occurs when the combined result of two developing agents is greater than either one of them working alone.

As a developing agent, metol provides good low-contrast shadow detail but produces weak highlight density. It is also fast-acting. Hydroquinone, on the other hand, is a slow-acting developing agent, which, when used alone, is capable of creating strong highlights and high contrast images.

Combining metol with hydroquinone can, in some formulas, result in a developer that is faster than metol alone and produces contrast equal to, or greater than, that of hydroquinone alone. Developers of this kind are known as MQ (for Metol and Quinol).

The optimum quantity of metol to hydroquinone is said to be 28% metol to the total amount of hydroquinone in the formula.

The phenomenon of superadditivity is even more pronounced when Phenidone and hydroquinone are combined (PQ). Phenidone on its own is almost useless as a developing agent as it is fast-acting but produces extremely low-contrast negatives (an exception is the low-contrast developer, POTA, which is intended to produce low contrast negatives). By adding a comparatively small quantity to a hydroquinone developer, Phenidone retains its high activity and combines with it the higher contrast of hydroquinone. The optimum amount of Phenidone to hydroquinone is said to be 7%.

Under most conditions, Phenidone is about eighteen times more efficient than metol. An optimized PQ developer is 50% faster than a comparable MQ developer. However, this increased efficiency has its downside. PQ developers often have a tendency to produce more fog. Fortunately, this can be controlled by the addition of benzotriazole in the amount of 0.1 to 0.2 g/L (because of the difficulty of measuring small amounts, it is easier to use 5.0 to 10.0 ml of a 2% benzotriazole solution, Appendix 2: Chemicals). Finally, the higher the proportion of either metol or Phenidone, the lower the contrast of the negative or print. Conversely, the higher the proportion of hydroquinone, the higher the contrast.

Other superadditive combinations are pyro-metol, metol-ascorbic acid, Phenidone ascorbic acid, and Phenidone-glycin. The superadditive effects are similar, while the resulting negatives exhibit their own unique qualities.

Trouble in Paradise

From the above it would seem that the best developers to use are those that exhibit superadditive characteristics. Most general-purpose developers fall into this category, as do many other formulas. However, there is a flip side. Most developers that utilize this effect tend to yield greater high-value density than those that rely on one developing agent. A developer of the semi-compensating type using either metol or pyro alone in a solution of relatively low pH is capable of producing brilliant high values, full-scale mid-tones, and shadows, for example, Kodak D-23 and Kodak D-1/ABC Pyro.

With the average MQ or PQ developer, by the time the required shadow density is reached, the high-value densities may be too severe. On the other hand, stopping development just when the desired high values are reached may not produce sufficient shadow density.

For this reason, many photographers who use general purpose MQ or PQ developers use them as one-shot developers, diluted 1:1. This provides additional highlight compensation without greatly increasing the development time and without causing loss of emulsion speed.

Because superadditive formulas result in shorter development times, usually five to ten minutes, the advantage of prolonged development times, fifteen to thirty minutes, is often not appreciated by photographers accustomed to using superadditive developers. However, extended development in a semi-compensating developer, or developers of low pH or alkalinity, will often produce negatives of incomparable scale if photographers are willing to take the additional time.

Preservatives =

During the development process the developing agent is oxidized, rendering it useless. However, developers will oxidize even without the development process. To prevent this, or at least inhibit the rate of oxidation, a preservative is added to the developer.

By far the most commonly used preservative is sodium sulfite. Potassium sulfite is only occasionally used in highly concentrated formulas such as Ordinal. Sodium bisulfite is often preferred in pyro developers and in Phenidone concentrates (Appendix 3: Pharmacopoeia: Phenidone). Sodium bisulfite is often used in formulas that are divided into two solutions, as its weak acidity helps to inhibit the oxidation of the concentrated developing agent. When carbonate, contained in the "B" solution, is added to make a working solution, the bisulfite is immediately broken down into sulfite and bicarbonate, producing a useful buffering effect.

Potassium metabisulfite will sometimes be encountered in formulas. For photographic purposes, there is no practical difference between potassium and sodium metabisulfite except that the potassium salt is more expensive. They can be exchanged weight for weight in most formulas.

Accelerators (Alkali) =

As a rule, developing agents have very weak developing powers in an acidic or neutral solution and require the presence of an alkali, known as an accelerator, to make them practical for use. Without some form of accelerator, most developing agents would require several hours to reduce the silver halide. Even then, the results would be low contrast with excessive fog buildup. Adding an accelerator greatly reduces development time and increases the contrast.

There are three general categories of accelerator:

- Mild alkali—pH value around 8 to 10 (borax, sodium metaborate, and sodium sulfite)
- Moderate alkali—pH value around 10 to 11 (sodium carbonate, potassium carbonate, and trisodium phosphate)
- Caustic alkali—pH value around 12 (potassium hydroxide and sodium hydroxide)

Increasing the amount of accelerator in a developer will increase the contrast. This is because it creates a more active environment in which the developing agent can reduce additional silver halide in the exposed areas. However, too much accelerator will increase fog levels, necessitating the addition of bromide or some other form of restrainer. While paper developers should always contain some restrainer, when formulating a film developer it is better to decrease the accelerator rather than add more restrainer.

pH =

The pH of a developer plays a major role in how fast the developing agents will cause an image to be formed on film or paper. The higher the pH, the more active is the developer.

Also, the higher the pH, the faster a developer will oxidize. To prevent oxidation, developers often are stored in separate A and B solutions that are mixed just prior to use. Developers using caustic alkali should always be formulated in this manner. Developers containing easily oxidized developing agents, such as pyro, should also be stored this way, regardless of which accelerator is used.

pH Scale

The pH scale has a range from 1 to 14, the neutral point being pH 7. Any solution with a pH higher than 7 is considered alkaline; a pH lower than 7 indicates an acid. An example of an alkali would be laundry soap; an example of an acid would be lemon juice. Mild acids and alkalis fall close to 7 on the scale; stronger acids or alkalis are found at either end of the scale.

Although the differences between the pH values may seem small, remember that the pH figures are logarithmic values. This means that a solution of pH 10 is 10 times more alkaline than a solution of pH 9. Thus a small change in pH indicates a sizeable variation in alkalinity. An inexpensive meter that will enable you to monitor pH levels is the pHep® made by Hanna Instruments.

Here are some examples of the pH value of chemicals used in developing, as well as common liquids for reference:

14.0 – Sodium hydroxide (4%); liquid drain cleaner
13.0 – Sodium hydroxide (0.4%); liquid bleach
12.0 – Developers containing caustic alkali; soapy water
11.5 – Sodium carbonate (5%)
11.3 – Trisodium phosphate (1%)
11.0 – Ammonia solution
10.5 – Sodium metaborate; developers containing carbonate
10.0 – Milk of Magnesia
9.9 – Balanced Alkali (0.2%)
9.5 – Borax (0.1%)
9.0 – Alkaline fixer (8.5–9.5); fine grain developers, baking soda
8.0 – Sodium sulfite (5%); sea water
7.0 – Deionized water; potassium bromide
6.0 – Saliva
5.2 – Boric acid (0.5%)
5.0 – Black coffee
4.3 – Sodium bisulfite
4.2 – Fresh acid fixers
4.0 – Stop baths; tomato juice
3.0 – Grapefruit and orange juice
2.9 – Acetic acid stop bath
2.2 – Citric acid (2%)
2.0 – Lemon juice; vinegar
1.2 – Sulfuric acid (1%)
1.1 – Hydrochloric acid (3 to 4%)
1.0 – Hydrochloric acid secreted by stomach
0.0 – Battery acid

pH has another implication for photographers and that is: Acid and alkali neutralize each other. With the exception of Amidol-based developers, developing formulas are all alkali and almost all fixing formulas used today are acid. ***That is why if you place a print in an acid stop bath or acid fixer you cannot return it to the developer - it will neutralize the print developer.***

The opposite is also true. ***If you take a print (or negative) from an alkali developer and place it directly into an acid fixer, the fixer will rapidly become neutral in pH and no longer work.*** This is perhaps more serious than going the other way because all the prints and negatives that appear to be fixed while the acid fixer is becoming less active due to alkali contamination, will deteriorate in a relatively short time after processing.

Buffering =

A buffer acts to keep the pH of the solution fairly constant. A buffered developer will maintain a constant pH whether it is diluted 1:1 or 1:3. A non-buffered developer may change its pH as it is diluted. Most alkalis used in developers have some buffering ability.

Carbonate and sodium metaborate are the most stable alkalis. Borax does not buffer well against a rise in pH, and hydroxide loses its alkalinity rapidly as the solution is diluted.

Mild Alkalis =

Mild alkalis produce less contrast and take longer to work, but they remain stable for a longer period of time in a working solution, especially in large concentrations.

Balanced Alkali is a proprietary chemical of Eastman Kodak, and until recently it was known as Kodak ®. Balanced Alkali is more alkaline than borax and more easily soluble, but less alkaline than carbonate. As Balanced Alkali contains no free carbonate, there is no danger of carbonic gas bubbles being formed when an acid stop bath is used (see the next section, Moderate Alkalis). Balanced Alkali can be substituted for carbonate (Conversion Tables: Alkali Substitutions), and for almost all purposes it is identical to sodium metaborate.

A substitution for Balanced Alkali can be made by mixing sodium hydroxide with borax, decahydrate (Appendix 3: Pharmacopoeia: Balanced Alkali).

Borax is the mildest common alkali. It finds its widest use in low-contrast and fine-grain developers. Decahydrate is the preferred form. Sodium sulfite, though most often used as a preservative, can also be used as a mild alkali. In Kodak D-23 it serves both purposes.

Moderate Alkalis =

Sodium carbonate, generally referred to as “carbonate,” is available in three forms: anhydrous (also known as desiccated), monohydrous, and crystalline. The difference between the three concerns the number of water molecules attached to each molecule of sodium carbonate.

Anhydrous has no water molecules attached, monohydrous has one, and crystalline has ten. The more water molecules there are, the greater the weight of chemical necessary to provide the same activity in solution. For example, the equivalent of 35.0 grams anhydrous would be 41.0 grams of monohydrate (Conversion Tables: Sodium Carbonate Conversion Table).

Anhydrous, having no water is quicker to absorb moisture from the air and must be stored in an airtight container to prevent deterioration. The crystalline form, which tends to lose its water molecules rather rapidly, is rarely seen in current photographic practice. With its single molecule, the monohydrous form is the most stable of the three and for this reason the most desirable.

Carbonate has one important drawback. When a large amount is used carbonic gas bubbles can form in the emulsion of either film or paper when transferred to an acetic stop bath, resulting in pinholes and/or reticulation. Using a less acid stop bath, such as Kodak SB-1 Non-hardening Stop Bath or a running water bath, should prevent this from occurring.

Potassium carbonate is available in both anhydrous and crystalline forms. The crystalline contains 1.5 molecules of water and a small amount of bicarbonate buffer, depending on the grade. The potassium salt readily absorbs water from the air and must be kept in airtight containers.

Potassium carbonate is far more soluble than sodium carbonate, hence its use in highly concentrated solutions. The two should not be interchanged. Trisodium phosphate (TSP) can often be used as a moderate alkali.

Caustic Alkalis =

Potassium and sodium hydroxide are far more energetic than the alkali carbonates and are used only when a powerful, fast-acting developer is required. Developers compounded with caustic alkalis have poor keeping properties and are soon exhausted. The only practical difference between potassium and sodium hydroxide, as far as photography is concerned, is that 10 parts by weight of sodium are the equivalent of 14 parts by weight of potassium. Also, potassium hydroxide is more soluble, meaning more will go into solution than sodium hydroxide. The limit of sodium hydroxide in water is 50%; the limit for potassium hydroxide is somewhat higher.

Phosphates =

Sodium and potassium phosphate approach the pH of the hydroxides without being as dangerous to handle. Although technically speaking phosphates are not true alkalis, they can be considered as replacements for hydroxides when high alkalinity is desired. One reason phosphates have been little used is that they can cause a scum if the film is plunged directly into a fixer that contains alum hardeners. Since the use of alum hardeners is waning, this may no longer be a major concern. In powder form, the phosphates appear to be less stable than other alkalis.

RESTRAINERS

Restrainers are necessary to prevent excess fog. With film developers, this primarily means chemical fog. With paper developers, restrainers are used to retard both chemical and safelight fog.

Restrainers should sparingly be used in film developers. Some photo chemists recommend that they not be used at all. According to photo chemist Bill Troop, "A film developer should not need to use a restrainer - if it does then the alkali is too strong." Even so, most film-developing formulas rely on restrainers, partly to prevent fog and partly as "insurance" against errors in formulation. Whereas a degree of base fog is permissible in a negative, no amount of fog, which would show up as gray highlights, is acceptable in paper. For this reason, paper developers always require restrainer, often in significant amounts.

Potassium Bromide

Potassium bromide, usually referred to as “bromide,” is the primary restrainer found in most developers. Bromide has the effect of holding back the overall action of the developer, reducing the effective sensitivity of the film, and diminishing the amount of useful density created in the shadow areas. By inhibiting the reduction of silver halide, bromide also acts to increase contrast. This action varies with different developers.

As film is developed, soluble bromide is produced and passes into the developer solution. This buildup of bromide adds to the already existing restrainer. If too much bromide is initially present, the combined amounts can considerably affect the contrast and effective sensitivity of the film.

Another consequence of this reaction is “bromide drag,” which occurs when either too much bromide builds up in the developing solution or agitation is unidirectional, causing streaks across the negative. This can be prevented by sufficient agitation, altering the direction of agitation, and the use of “one-shot” developers or the proper replenishment of developers before use.

Bromide is generally used in paper developers when a warm or neutral tone is desired. The more bromide, the warmer the tone, though too much bromide will inhibit development in the shadow areas and fogging may occur.

Benzotriazole (BZT)

The anti-fogging effects of BZT are greater than bromide, especially in developers of high pH. As a result, BZT is especially useful for salvaging outdated papers or when blue-black tones in prints are desired.

For salvaging outdated papers, mix a 0.2% solution (2.0 grams in water at 125F / 52C to make 1.0 liter). Add 15.0 ml of this solution to every liter of developer. If 15.0 ml does not do the trick, keep adding 15.0 ml at a time and make tests until you get a clear paper without fog.

To test, develop a small piece of unexposed paper for the full time; after fixing, when the paper is held up to a white surface, such as the back of another piece of paper, it should show no signs of gray. It is advisable with all old paper, even those not exhibiting fog, to keep development times between 45 seconds and 1.5 minutes (***the longer paper develops, the more likely it will exhibit fog***).

While BZT is often used in PQ formulas, especially those of medium to high alkalinity, bromide is a superior restrainer in PQ formulas of low alkalinity. As a substitute for bromide, BZT is generally used at 1/10th the solution concentration of the bromide.

Potassium Iodide

Although it is recommended by no less an authority than Geoffrey Crawley, former editor of the British Journal of Photography and formulator of FX and Paterson proprietary developers, potassium iodide has not been thoroughly investigated for its use as a restrainer. However, what little research has been done indicates that it is superior to potassium bromide. As a substitute, it is usually recommended to use 1/10 to 1/100 the weight of bromide. Iodide can also be used in combination with bromide.

OTHER ADDITIONS TO DEVELOPERS

Water Softener

When hard water is used for mixing developers, milkiness is sometimes produced. This is caused by the action of alkali and sulfite on the lime salts in the water. If the lime is excessive, a precipitate of calcium carbonate and sulfite may be deposited on film. In areas of hard-water concentration, it is best to compound developers using distilled, deionized, or demineralized water. However, if none of these is available, a water softener can be added directly to the developer. Do not add a water softener unless it is absolutely necessary as it will change the pH balance of the developer.

If a water softener is required, use a small amount of sodium Hexamita phosphate, available as the proprietary compound Calgon™. One part per 1,000 (1g/L) should be sufficient, except for very hard water, in which case the amount can be increased up to 3 g/L. Always dissolve the water softener before adding the developing ingredients.

OTHER CONSIDERATIONS FOR DEVELOPERS

All developing agents in developer solution will oxidize when exposed to air. MQ and PQ developers that contain high concentrations of sodium sulfite are slower to oxidize than most other developing agents. High-energy developers containing caustic alkali, developers containing pyrogallol, pyrocatechin, catechol, amidol, and many others, oxidize quickly. These should be used immediately upon diluting to a working solution.

Dark brown or amber glass bottles are best for storing developers. Always fill the bottle to the top in order to prevent oxidation. This can be achieved through the addition of glass marbles that take up extra space. However, do not use glass marbles with developers with high acid or alkali content (Appendix 2: Chemicals: Dos and Don'ts).

CREATING YOUR OWN FORMULA

The Darkroom Cookbook is meant to be a point of departure for photographers desiring to take control of their craft. At any time, you should feel empowered to “interpret” any formula, design a new one, or adapt an existing one to a new purpose. In doing so, keep these six aspects of the process in mind:

1. The developing agent - its nature, concentration, and, in cases where several are used, the ratio between them.
2. The alkali or accelerator - its nature and concentration. Also, keep in mind with film that if you have too much fog, you have too much alkali. Reduce the alkali content before adding restrainer.
3. The restrainer - its type and quantity.
4. The preservative can greatly affect both the graininess and compensating effect of the developer.
5. The percentage of each component in the formula.
6. Never compare stock solutions of formulas. Compare working dilutions only.

The following is a good way to teach yourself how to manipulate developing formulas and the effect of different chemicals. Start with a general-purpose paper developer, such as Kodak D-72, and dilute as you would for a normal print. Choose a full-scale negative that prints well on grade-2 paper or with a #2 Variable Contrast filter. Make a good print and write "control" on the back. Make thirteen more identical prints and put them in a light-tight box without developing them. The prints do not have to be large; 4X5 inches or 5X7 inches will suffice.

- Mix a fresh batch of developer using only the metol and sulfite in 1.0 liter of water, then dilute and develop the first print for the same time as the control print. Add the carbonate and develop the second print. Add the bromide and develop the third print. Be sure to mark the back of each successive print with a number, such as "1", "2," and so on.

- Mix a fresh batch of developer this time using only the hydroquinone and sulfite in 1.0 liter of water, diluting as before, and then adding the other chemicals in succession. Be sure to mark the back of each print.

- Mix a fresh solution of D-72 only this time use half the amount of carbonate (40.0 grams), and develop another print. Then add 80.0 grams more carbonate to bring the amount to half again more than normal (total carbonate 120.0 grams). Add 40.0 grams more carbonate to double the normal amount (total carbonate 160.0 grams).

- Mix another solution of D-72 only this time use the normal amount of carbonate (80.0 grams) and no bromide to start with. Then add bromide to bring the total to 1.0 gram, 2.5 grams, and finally, 4.0 grams.

Compare each print to the test print and become familiar with the results. You can repeat this test with any paper developer. Doing this test in its entirety will familiarize you with the full range of effects and controls possible with any developer. It will also help you learn how to create your own formulas.

Ascorbic Acid: Developing Agent or Anti-oxidant? - (Patrick Gainer)

We know it as Vitamin C, an anti-oxidant essential to human life. Photographers think of it as a secondary developing agent in superadditive pairs such as Metol-Absorbate or Phenidone - Acerbate. These have been known for years but recently made popular by Kodak XTOL film developer.

The traditional synergistic or superadditive developer solution has four active ingredients: two developing agents, sulfite, and an alkali. We tend to take the sulfite for granted for control of grain and/or pH, but don't try leaving it out as it is also the preservative (anti-oxidant) which keeps the developer from going fl at part way through development. Sodium sulfite is used as the preservative in nearly all developers, film or paper.

But a photographic developer can be made without sulfite by substituting ascorbic acid, using Phenidone or metol, ascorbic acid, an alkali, and water. I learned of this quite by accident in 1993 when I ran out of sodium sulfite. The nearest supplier was a 100 mile round trip! Knowing that ascorbic acid is an anti-oxidant and having some in my medicine closet I decided to chance it. My escapades that day were described in Darkroom and Creative Camera Techniques, Nov/Dec 1994 (reprinted on Ed Buffaloes's web site, www.unblinkingeye.com/articles, under Film and Film Developers:

Vitamin C Developers).

A simple formula to try is:

Hot water,	250.0 ml
Ascorbic Acid ,	2.0 g or 1/2 tsp
Metol,	0.2 g or 1/16 tsp
Sodium Carbonate,	5.0 g or 1 tsp
Water to make	1.0 liter

Use this formula as if it were D-76 undiluted.

For photographic use it is best to purchase either ascorbic acid or its isomer (mirror image) erythorbic acid. There are other perfectly legitimate forms of Vitamin C that are not legitimate for photo use, such as calcium ascorbate, especially if it is to be dissolved in propylene glycol or triethanolamine.

Three Long-Lasting Single-Solution Sulfite-Free Developers (Patrick A. Gainer)
PCTEA

PCTEA is a Phenidone-ascorbic acid developer with triethanolamine (TEA for short) activator. Using this formula, I can't find the grain in HP5 or TMAX 400 at less than a 20-power enlargement.

Even in very thin negatives of low contrast, shadow detail is still apparent. The following formula may be scaled up to any desired amount.

TEA,	100.0 ml
Phenidone,	0.5 g
Ascorbic acid,	9.0 g

Heat the solvent to 250F/121C in a water bath, such as a double boiler with the top part covered to prevent condensation of water vapor into the developer concentrate. It won't boil, but some steam may be given off if there is any water in the solvent mixture.

Steam will arise when the powdered ingredients are added, which I presume to be water produced in the reaction between the ascorbic acid and part of the TEA. Once the powders have dissolved they will remain in solution and as long as water is kept out of the stock it will not oxidize by exposure to air.

NOTE: Metol is not soluble in this solvent.

You can play with the dilution. I recommend 1 part of concentrate to 50 parts of water for starters.

Dilute 1:50 and use the same initial developing times as D-76 1:1.

CATPTEA

The name does not refer to its appearance or its bouquet. I just couldn't resist. This is a staining developer containing catechol and Phenidone. You may use hydroquinone in place of the catechol if you like to save money. They are both dihydroxybenzene, the difference being in the location of one of the OH groups on the benzene ring. Both are staining developers.

TEA,	100.0 ml
Catechol,	10.0 g
Phenidone,	0.25 g

Heat as for PCTEA. Dilute 1:100 for use. The negatives will look thinner and of lower contrast to the eye than to the printing paper, and lower in contrast to VC than to #2-graded paper. If you use a 10% sodium sulfite solution to dilute the stock, you will have a developer similar to D-76.

You can experiment with different proportions of stock, sulfite solution, and water.

PPTEA

This name does not refer to its appearance but to the fact that pyrogallol and Phenidone are the developing agents.

TEA,	100.0 ml
Pyrogallol,	10.0 g
Phenidone,	0.25 g

Heat as for PCTEA. Again, the negatives will be stained and look thinner and less contrasty to the eye than to the paper, and of lower contrast to VC than to graded paper.

Effects of Adding Sulfite

There is no sulfite in either the stock solution or the working solution. There are, in fact, no inorganic compounds in the stock solution. There is nothing to keep you from adding sulfite to the working solution, but try it first as is. If you add a tiny amount of sulfite to CATPTEA or PPTEA, say one-quarter teaspoon to the liter, its activity will increase because of the activation by the sulfite of the superadditivity between Phenidone and hydroquinone, catechol or pyrogallol. Graininess will also increase. It will still be a staining developer until you add a fair amount of sulfite.

Print Developers

"They say my print quality is bad. Darling, they should see my negatives." (Lisette Model)

DIFFERENCES BETWEEN PRINT AND NEGATIVE DEVELOPERS

Print developers are far more forgiving than negative developers. When formulating and mixing print developers it is possible to be off a certain percentage and still obtain pleasing results; indeed, you might like the results better!

While there are many similarities a print developer differs from a film developer in the following ways:

- A print developer must be sufficiently active and concentrated so that development does not take an inconveniently long time.
- The composition of the print developer affects the image tone of the paper.
- Print developers can affect the inherent grain structure of the paper which can, in turn, affect the tone of the paper, especially when the paper is subjected to further toning processes.

- The action of the developer should be as uniform as possible over a long printing session to avoid having to re-mix fresh developer every few prints. This is also important when creating editions of prints where both tone and tonality need to be consistent.

- It is necessary to have sufficient restrainer present to avoid veiling (fog), otherwise the whites in the print will be gray.

PRINT DEVELOPER COMPOSITION

The composition of a print developer is usually as follows:

- Developing agents. The most common print developing agents in use today are metol or Phenidone, plus hydroquinone. In recent years glycin has regained some popularity.

- Preservative, which is always sodium sulfite.

- Alkali (accelerator) is nearly always sodium carbonate, with potassium carbonate often substituted for warm tone results. Sodium hydroxide is occasionally used, mainly to increase contrast; sodium metaborate is found in universal developers.

- Restrainer, which is usually potassium bromide or benzotriazole.

THE USE OF RESTRAINER IN PRINT DEVELOPING FORMULAE

The amount of bromide or organic restrainer in a print developer should ideally be optimized for the particular paper being used and the image tone desired. For example, in order to achieve a cold tone the print developer should contain the smallest amount of restrainer that does not allow the whites of the particular paper to fog. Similarly, in order to achieve a warm tone, the print developer should contain the largest amount of bromide that will not lead to greenish tones. This optimization is possible when the correct amount of restrainer is determined by experimentation with a specific paper. This can be achieved by adding small amounts of restrainer to the developer until the desired result is obtained. Once determined, the formula can be replicated.

TRAY LIFE OF PRINT DEVELOPERS

As print developer is used, each print adds bromide to the solution, removes a little organic anti-foggant if one is present, and absorbs some of the developing agent. Although it may not be noticeable from one print to the next, some speed is lost, contrast is increased, and development time is lengthened. In addition, the excess bromide in a print developer can often change the image tone to a warmer hue.

One method of making a print developer less sensitive to bromide is to formulate it with a large amount of potassium bromide already in solution. Then the small amounts that are added with each print become a very small percentage of the total. Ansco 130 is formulated in this manner. In addition, Ansco 130 is highly resistant to oxidation because of the use of glycine as one of the developing agents. This further reduces the tendency for streaking or staining when the developer is close to exhaustion.

There is no rule for how long a print developer will last as this depends largely on the formulation, as noted above with Ansco 130, which has an exceptionally long life in working solution. As a rough guide, however, 15 to 20 8X10 inch prints per liter is not unusual for most print developers.

It is also possible to determine the life of a developer by taking note of how long the image takes to appear in the first print. When the time is noted to be slightly more than double it is time to toss the developer (for example, if the first print takes 15 seconds for the image to appear then the developer should be tossed or replenished when it begins to appear at about 35 seconds). However, to extend the working life of a print developer, it is possible to add 30.0 to 45.0 ml per liter of stock solution to the working solution in the tray (the actual amount is not critical but use 30.0 ml as the minimum). This should only be done once in a print session and the developer should be discarded at the end of the session. This is also not a good idea when making prints which are part of a limited edition from a single negative.

Printing Limited Editions

The fact that print developers are not consistent over their working life is not usually a problem as small adjustments in density or contrast can be made by inspection. The exception is when a limited edition of prints from a single negative is being made. When a print edition is being made it is important that the print developer have even tonal and contrast characteristics over its working life. One way to accomplish this is to change the developer often.

Another is to use a developer that has a high capacity, such as Ansco 130. Combining the two methods is the best.

MQ VERSUS PQ PRINT DEVELOPERS

There are a number of differences between Phenidone/Hydroquinone (PQ) and Metol / Hydroquinone (MQ) print developers, but none of them are significant enough to cause one to be preferred to the other. Perhaps the most important difference is the longer and more consistent working life of a PQ developer. This is because Phenidone is less sensitive to bromide so the build-up of bromide in solution has little effect on its activity. However, it should be noted that the organic restrainers found in high pH PQ developers are carried off by the print. While this will not affect the activity of the developer it will have some affect on the overall contrast of succeeding prints.

Another difference is that it is not easy to formulate a higher-than-normal contrast developer using Phenidone. At the same time, it is relatively easy to adjust the contrast, high or low, of a MQ developer, making the MQ combination easier to work with when using or formulating a print developer.

It has already been mentioned that when formulating PQ developers of high pH an organic restrainer should be used. Conversely, when formulating PQ developers of low to moderate pH potassium bromide should be used. This is because while Phenidone is not very sensitive to bromide at high pH, it is sensitive at low to moderate pH. PQ developers often produce a colder image tone on prints. This is not caused by the Phenidone per se but is the natural effect of the organic restrainers necessary in high pH Phenidone print developers.

When printing with Resin Coated (RC) papers the induction period may be reduced to a few seconds, and the full development time to less than 60 seconds if an active PQ developer is used.

BROMIDE AND CARBONATE

To increase the flexibility of MQ and PQ print-developing formulas, keep a bottle of carbonate solution and a bottle of 10% bromide on your darkroom shelf. I learned this trick from photographer Edna Bullock, who learned it from her husband, Wynn Bullock. Wynn used this technique with Ethol LPD® paper developer.

Carbonate Solution

Adding carbonate solution to paper developer will increase the speed of the developer and create the appearance of greater contrast through stronger and richer blacks. Start with 50.0 to 100.0 ml to each liter of paper developer. As much as 200.0 ml can be used per liter, but beyond that your highlights may begin to fog.

To make a carbonate solution, dissolve 60.0 grams of carbonate in 750.0 ml of water and add water to make 1.0 liter.

If you intend to gold-tone a print for blue tones, do not add too much carbonate solution as it will make it difficult to secure a brilliant blue with gold chloride toner.

10% Bromide

With paper developers, adding a solution of 10% bromide will help prevent fog and slow the speed of excessively fast papers (allowing longer printing times for dodging and burning). Additionally, it will give clearer highlights, slightly extending the contrast range of the paper.

With shortened development times it will produce brownish to olive-brown tones with some warm-tone papers. Finally, it will enhance or increase warm tones by restraining development.

Add 15.0 to 25.0 ml of 10% bromide to 1.0 liter of developer. You can add more, but even though bromide helps to prevent fog, after a point it will actually cause fogging. This usually appears as a subtle graying of the highlights.

A simple test for chemical fog is to take a piece of unexposed paper and cut it into four parts. Develop and fix the first, as a control, for the normal time. Then, as you increase the amount of restrainer or anti-foggant, develop additional pieces and compare them to the control print. As long as they are as white as the control, more restrainer may be added.

To make a 10% bromide solution, add 100.0 grams of potassium bromide to water to make 1.0 liter.

A Perfect Balance The combination of carbonate solution and 10% bromide balance each other to achieve the best possible results. The increase in speed gained from using carbonate balances the decrease in speed caused by bromide. At the same time, highlights are enhanced by the restraining properties of the bromide, while blacks become stronger and richer with the carbonate.

When using them together, add one part bromide to three parts carbonate. It is not a good idea to add bromide and/or carbonate from force of habit. It is better to begin with an un-manipulated developer, observe the results, and then determine if one, the other, or both are needed.

Chemicals

(“Photography, in the final analysis, can be reduced to a few simple principles. But, unlike most arts, it seems complex at the initial approach.” - Ansel Adams, 1948)

Most of the chemicals used in black and white processes are safe and biodegradable. A few, such as selenium, pyrogallol, pyrocatechin, sodium hydroxide, and hydrochloric acid, require careful handling and disposal. Throughout The Darkroom Cookbook specific warnings and instructions will be given where appropriate.

Appendix 3: Pharmacopoeia, contains descriptions of chemicals, including most of those used in this book. Knowledge of these chemicals and their use will be of great advantage in manipulating formulas. This chapter is a general overview for those not familiar with handling chemicals.

OBTAINING CHEMICALS

Some of the chemicals can be obtained from photo suppliers. Less common chemicals, such as amidol and pyrogallol, can be obtained from various chemical suppliers. A few suppliers even specialize in photographic chemicals. Not all chemical suppliers will sell directly to the public. Some that do are listed in Resources.

NOMENCLATURE

Manufacturers often give their own trade name to the same chemical. For example, the developing agent monomethyl-p-aminophenol sulfate has been known as Kodak Elon, DuPont Rhodol, Defender Veritol, and others. Throughout The Darkroom Cookbook, this widely used chemical will be referred to by its most common name, metol.

Spelling also varies between the U.S. and Great Britain. The British spelling of sodium sulfite is sodium sulphite, and sodium sulfate is spelled sodium sulphate. The Darkroom Cookbook will use the U.S. spelling.

CHEMICAL CLASSIFICATION

Chemicals come in different grades or classifications: analytical reagent (AR); pharmaceutical or practical; and technical or commercial.

● AR. Chemicals of AR quality are used primarily for analytical and testing purposes. Such chemicals meet the highest standard for purity and uniformity. Though they may be used for photographic work, they are the most expensive and not required. In the United States, AR-quality chemicals are labeled ACS (American Chemical Specification) and in the United Kingdom ANALAR™ (Analytical Analyzed Reagents). ANALAR is a trademark of ANALAR Standards, Ltd., a subsidiary of British Drug House Chemicals, Ltd., a leading authority on international chemical standards.

● Pharmaceutical or Practical. These chemicals meet the specifications of the U.S. Pharmacopeia (USP) or the National Formulary (NF). USP/NF quality chemicals are approximately 97% pure and can be used for almost all photographic work. In Great Britain, they are labeled either BP (British Pharmacopeia) or BPC (British Pharmaceutical Codex).

● Technical or Commercial. These chemicals are primarily intended for use in manufacturing processes (e.g., making laundry detergents). In a few instances it may prove economical to use such chemicals, but generally speaking, they cannot be recommended for photographic work.

ANHYDROUS (DESICCATED), MONOHYDRATE, AND CRYSTALLINE

The terms anhydrous (desiccated), monohydrate, and crystalline are often a source of confusion. They refer to the various hydrate forms of some chemicals.

- Anhydrous, and the older name desiccated, means “without water.”
- Monohydrate means that one water molecule is attached to the chemical’s molecule.
- Crystalline means that as many water molecules as possible are attached to the chemical’s molecule.

Monohydrate chemicals are generally the most stable. Anhydrous chemicals will try to absorb water from the air to become monohydrate. Crystalline chemicals will try to release their water to the air to become monohydrate. Due to these tendencies it is important to store anhydrous and crystalline chemicals in airtight bottles to maintain their hydrate state.

The water bonded to the chemical makes the molecule weigh more. The extra weight is only water. In practice, this means that if a formula calls for an anhydrous chemical you will need more monohydrate or crystalline chemical to make the same working concentration.

You can use the Sodium Carbonate Conversion Table at the end of the book if you have a different hydrate form than called for in the formula.

WEIGHTS AND MEASURES

Two systems of measurements are in common use for measuring and weighing: U.S. customary, and metric. U.S. customary utilizes grains (g), ounces (oz.), and pounds (lb.); metric uses grams (g) and milliliters (ml).

In this 3rd edition of The Darkroom Cookbook, formulas are only given in metric measurements.

You do not need to know anything about the metric system. It’s only numbers. Once you get used to it you will find it easier to calculate changes in measurements.

For example, which is easier to add: 5.0 grams plus 10.0 grams (metric), or 73.0 grains plus 145.0 grains (U.S. Customary)? Not convinced? Okay, try liquid measures.

You need to make a 15% solution. Fifteen percent of 1000.0 ml is 150.0 ml. Fifteen percent of 32.0 oz. is, uh . . . let's see . . . 10% of 32.0 oz. is 3.2 oz., half of 3.2 is 1.6. Then 1.6 plus 3.2 is 4.8! That's it! Fifteen percent of 32.0 oz. is 4.8 oz! I suggest you get used to working with metric measurements if you're going to mix your own formulas.

Even so, you may occasionally come across an older formula given in U.S. customary units. Should you wish to convert from one to the other you will want to use the compound conversion chart found under Conversion Tables at the back of the book. This is because the figures are not directly interchangeable between U.S. customary and metric, because 1.0 liter of water does not exactly equal 32.0 oz. Therefore, they must be specially compounded to be equivalent.

PREPARING FORMULAS

Before attempting to mix any formula, read and follow all handling and safety instructions listed for the chemicals. Always wear protective equipment such as safety glasses, a plastic apron, rubber gloves, and a mask to avoid allergic reactions, burns, and irritation to the skin or lungs.

Refer to Appendix 1: Safety in Handling Photographic Chemicals for explicit safety instructions and for a list of 24-hour poison center hotlines.

Dos and Don'ts

- Never place raw chemicals directly on the scale. Chemicals can be weighed by placing a piece of filter paper on top of the pan, or a non-pleated paper cup, such as a Dixie® cup. The second method is preferred, as there is a tendency, when using paper, for the chemical to spill over the sides and make a mess. Instead of a paper cup, reusable plastic weighing cups can also be purchased from chemical suppliers.
- When mixing an acid, always pour the acid into the water. Do not pour water into the acid, as splattering can occur, causing dangerous burns. Be sure to wear eye protection.
- Use a funnel when pouring solutions into bottles.
- Tightly secure the top and label the bottle with the solution's name and date. Most developers keep for only a few months.

- Do not prepare formulas in the containers or tanks in which they are to be used. Glass or porcelain jars, wide-mouthed glass bottles, plastic beakers, or graduates are suitable for mixing.
- Never use metal other than stainless steel. In particular, do not use iron, copper, aluminum, or tin.
- Although solutions may be shaken to dissolve the ingredients, stirring is preferred, as shaking causes oxidation. When adding water do so slowly and, whenever possible, indirectly (i.e., allow the water to run down the wall of the mixing container rather than directly into the liquid). This will help to slow the rate of oxidation.
- Keep a record of what you do so you can adjust and customize the formulas.

Weighing Chemicals

A set of plastic or stainless steel measuring spoons will facilitate transferring chemicals from the bottle to the scales. They will help to prevent wasteful spills, which can cause contamination. Do not overfill the spoon; transfer a little at a time to prevent spilling.

Begin by placing the scale on a level, protected (e.g., newspaper-covered) surface and zeroing it. Place a weighing cup in the middle of the balance pan. If you are using a triple beam balance without a tare weigh the cup first and subtract its weight from that of the chemical. When using a double-pan scale place the same size cup in both pans so their weights will cancel each other.

Have all the chemicals to be used at hand and in the order of use. Use a clean cup and spoon for each chemical to prevent contamination. Immediately recap the bottles to avoid confusion, spills, or contaminating one chemical with another.

A convenient method for weighing small amounts of chemicals is to place them on precut pieces of paper. Write the name and weight of each chemical on the paper, and arrange the chemicals on the mixing bench in the order of use. For amounts over 20.0 grams, use a weighing cup instead.

Order of Dissolving

Unless otherwise specified, always dissolve the ingredients in the order given. In developers, the sulfite is usually dissolved first because most developing agents are easily oxidized in water without this preservative.

An exception is metol, which is only soluble with difficulty when mixed in solutions containing a high concentration of sulfite. Therefore, when mixing developers that contain metol you should dissolve the metol before the sulfite. This has a minimal effect on the keeping properties of the developer as metol is not easily oxidized. Even so, many workers prefer to dissolve a pinch of sulfite before dissolving the metol, to ensure against oxidation. The small amount of sulfite can either be taken out of the measured amount or ignored as it is usually insufficient to upset the balance of the finished developer.

A good rule to follow in preparing developers is to make certain that each ingredient is completely dissolved before the next is added. Always begin with at least a quarter, or even a half, less water than called for by the formula. When all the chemicals have been dissolved, add cold water to make the required volume.

Water

Unless a formula specifically calls for distilled water, in most cases tap water can be used.

Even when distilled water is indicated, good quality, filtered tap water will usually suffice. A notable exception is those formulas which call for the use of pyrocatechin (catechol) or pyrogalllic acid (pyro or pyrogallol). In areas where the water is very hard, it can be treated with sodium hexametaphosphate, or Calgon. Three g/L should be added before the other developing agents. EDTA, ethyl enediaminetetra acetic acid, can also be used, but it may speed up the rate of aerial oxidation of the developing agents, possibly causing diachronic fog.

If neither Calgon nor EDTA is available, an alternative method is to allow the water to settle overnight then decant the clear liquid, preferably through filter paper.

This procedure, while inconvenient, is sufficient for most developers.

Percentage Solutions

For convenience, and when the amount of a chemical may be too small to be weighed accurately, the amount is often given as a percentage solution. This can be simply stated as how many grams of a chemical are dissolved in 100.0 ml of water. For example, a 10% solution has 10.0 grams of a chemical dissolved in 100.0 ml of water. Regardless of the amount used in the formula, the percentage is always the same. That means that every 10.0 ml of a 10% solution contains 1.0 gram of the chemical. If a formula requires 2.0 grams of chemical, use 20.0 ml of the percentage solution.

The following is an example of the use of percentage solutions. Suppose the formula calls for:

Potassium ferricyanide,	5.0 g
Potassium bromide,	1.5 g
Water to make	1.0 liter (1.0 liter = 1000 ml)

If we start with stock solutions of 10% potassium ferricyanide and 10% potassium bromide, we can quickly make our solution by multiplying the dry amount by 10 and taking:

Potassium ferricyanide,	10% solution, 50.0 ml
Potassium bromide,	10% solution, 15.0 ml
Water to make	1.0 liter

It is easy to see the advantage of this method, especially for chemicals that are often used in small amounts (e.g., Phenidone, potassium bromide, benzotriazole).

When mixing percentage solutions start with less than the total volume of water. After the chemical is fully dissolved, add the remaining water to make the required volume.

Formulas in Parts

Many formulas are given in parts. Parts can be converted into the equivalent number of grams and milliliters. For example, a formula calling for “1 part A to 1 part B to 1000 parts water” can be translated as “1.0 ml of A, 1.0 ml of B, to 1000.0 ml of water.”

Often formulas in parts will be written as 1:1 - 1000, or 1:1:1000 or 1:1 to 1000 ml.

Whichever way it is written, it comes out the same. The important point is to make sure that all the units are in the same system of measurement, either metric or U.S. customary units; in other words, grams with grams, ounces with ounces. This is also important when both liquid and solids are indicated in “parts.” Be certain that solid ounces go with liquid fluid ounces and that solid grams go with liquid milliliters.

- See Details in the Pharmacopoeia Paper -